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LEAD ZIRCONATE TITANATE (LZT) CERAMICS.(U)
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LEAD ZIRCONATE TITANATE (LZT) CERAMICS

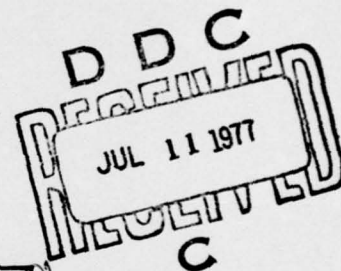
Annual Summary Report
to the
Office of Naval Research

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Submitted by

J. H. Rosolowski, R. H. Arendt and J. W. Szymaszek

June 1977



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SUMMARY

This report covers the first year's work on a program aimed at developing a better understanding of the mechanisms whereby the methods of powder preparation, processing and sintering control the microstructure of lead zirconate titanate (LZT) ceramics as well as their electric and piezoelectric properties. The effort was primarily directed toward developing a molten salt synthesis method for producing homogeneous, fully reacted LZT powders including all important property modifying additives such as Sr, Fe and Nb. The method involves reacting a mixture of powders of the components together with a eutectic NaCl-KCl mixture at a temperature where the salt is molten. A detailed procedure for LZT synthesis by this method is given.

Powders over a wide range of composition were successfully synthesized. Their X-ray diffraction characteristics and particle size distribution are discussed.

Ceramics were made from the powders using a common procedure for all. Their properties were compared to values obtained from the literature and found to be generally similar except that ceramics made from the molten salt synthesized powder characteristically showed a significantly lower dissipation factor and higher mechanical Q.

Powder for a reported slow aging composition containing Ca and Mg was prepared. The results indicated that Ca was soluble to $< 1/10$ and Mg to $< 1/2$ of the values specified in the nominal composition formula.

LEAD ZIRCONATE TITANATE (LZT) CERAMICS

J. H. Rosolowski, R. H. Arendt and J. W. Szymaszek

I. INTRODUCTION

This report covers the first year's work on a program aimed at developing a better understanding of the mechanisms by which the methods of powder preparation, processing and sintering control the microstructure of lead zirconate titanate (LZT) ceramics as well as their electrical and piezoelectric properties. The technological motivation for undertaking such a study arises from the difficulties manufacturers of LZT ceramics experience in producing transducers to rigid specifications, as for Navy applications. These difficulties result from the sensitivity of final properties to the sintering conditions coupled with the fact that each lot of powder generally behaves in a different manner. The scientific motivation for the study comes from its anticipated contribution to knowledge about powder characterization and the phenomenology of sintering in general.

Commercial LZT powders are prepared by calcining a mixture of the component oxides, or compounds such as the carbonates that decompose to oxides on heating in air. The formation of the compound LZT under these conditions is controlled by solid state diffusion across inter-particle contacts. Intermediate compounds are known to form during this process⁽¹⁾. The degree to which the reaction goes to completion locally in a given time depends intrinsically on the particle size and calcination temperature. These factors, as well as the perfection of the initial mixing of the reactants, also control the homogeneity of the product powder.

The observation that ceramics having different properties are obtained when different powder lots are processed and fired under nominally identical conditions suggests that incomplete reaction and inhomogeneity are indeed common properties of commercial powders. Evidence in support of this view is also available in the form of the common observation that calcined powders contain up to several weight per cent of unreacted ZrO_2 ; also, in a controlled experiment it was found that the density of ceramics depended on the temperature at which the powder from which they were pressed was calcined⁽²⁾.

Since the attainment of the objectives of the proposed program of investigation depends to a great degree on having available LZT powders that behave reproducibly when processed into ceramics, the first task undertaken was to develop a technique for producing such powders having compositions of technological interest. The technique chosen for development was that of molten salt synthesis. It is described in detail in the next section of this report.

The work during the first year was primarily devoted to developing the various steps in the powder synthesis so as to attain reproducible, homogeneous powders of varying Zr/Ti ratios and containing many of the dopant elements which are known to modify LZT properties. Throughout, it was attempted to develop the process along practical lines in the sense of allowing the possibility of scale-up from laboratory to commercial powder production. This report describes the powder synthesis technique as well as some of the physical characteristics of the powders that were made and the characteristics of the ceramics made from the powders.

Since the initial investigation was concentrated on the powder, no great effort was made to optimize the firing conditions to produce the best ceramic either from the point of view of density or of electrical properties. Rather, a standard method of producing samples was eventually adopted after some trials and these samples were compared with each other and to those reported in the literature. During the course of the work, however, certain aspects of powder processing and firing were seen to have an important effect on properties and these will be mentioned when appropriate.

II. MOLTEN SALT SYNTHESIS

The objective of the molten salt technique for synthesizing LZT is to effect a more complete reaction between the reactants and to produce a more compositionally homogeneous product powder by causing those reactants to be coated by a liquid in which the reaction to LZT occurs and from which the powder formed precipitates. This liquid medium, in which atoms diffuse rapidly, in effect brings large numbers of particles of the reactants into contact with each other so that they can react rapidly and completely. The homogeneity of the product is still dependent in the perfection with which the reactant powders are mixed but the dependence is much less than in the case of calcination where the reaction takes place at the contacts between particles. In addition, homogeneity is improved by the fact that in the molten salt the most thermodynamically stable compound forms directly instead of the end of a series of intermediates as in the case of calcination.

The development of this technique for LZT synthesis required several problems to be solved. The first was to choose the proper liquid composition. Although it is known that oxide reactions of the kind required can occur in molten ionic salts, the specific salt chosen must be such that the desired compound forms in it either alone or in combination with other compounds which may be easily removed later. After some trials, the choice was made to use an approximately eutectic mixture of NaCl and KCl. A fluoride melt (KF-KCl) was tried but a difficult-to-remove lead fluoride was formed with the excess lead introduced into the reactant mixture.

The other problems addressed were: to develop an effective way of mixing the reactants and the salts homogeneously; to develop a method for efficiently removing the excess unreacted PbO from the product powder; to develop a rapid method of separating the fine product powder from the water used to remove the salt. In addition, it was desired to develop the technique in such a way that it might be adopted for commercial use if the powder so made was eventually found to have desirably unique properties.

The recipe developed for producing LZT powder by the molten salt method follows. It can be scaled to make any desired quantity of product. The standard batch used in this work yielded 1 Kg of powder.

1. Prepare a reactant mixture containing the oxides of Pb, Ti, Zr, and any other desired cationic species which may be introduced as compounds that decompose to the oxides on

heating (e.g. carbonates, hydroxides, nitrates etc.). The components of the reactant mixtures should be in stoichiometric proportions except for Pb, which should be in excess (2 w/o has been used) to make up for vaporization losses and to drive the reaction toward the formation of LZT. The reactant powders should also be free of large, hard aggregates which might survive the mixing process.

2. Slurry the reaction mixture in H_2O at the rate of 1 ℓ H_2O /1 kg reaction mixture. Vigorous stirring should be employed to obtain a complete suspension. Settled material will generally not react completely.
3. When a well mixed slurry is attained, continue stirring and add 0.454 kg/1 kg reactants of both NaCl and KCl (0.908 kg total) as the solids.
4. Continue stirring until the mixture gels due to hydration (or carbonation) of the reactants. This gel will retain its homogeneity during subsequent processing.
5. Remove water by evaporation at 200°C using suitable vessels, Teflon lined being best.
6. React the dried cake in either Pt, Pt lined or stabilized zirconia crucibles (covered) at 1000°C for 30 min to 1 hr in an air atmosphere, then cool at any convenient rate to room temperature.
7. Dissolve the NaCl-KCl from the reacted cake using distilled or deionized water. The solubility of the salt mixture is 0.5 kg/ ℓ of water at room temperature. Glass vessels and a motor driven stirrer are adequate to use. The brick-like cake will disintegrate into a fine powder that contains no perceptibly aggregated material.
8. The supernatant solution will have a high ionic strength which will cause the product powder to flocculate and settle when mixing is stopped. The supernatant can therefore be nearly quantitatively decanted to allow repeated washings with distilled water. Washing should be repeated until a stage is reached where the supernatant will remain milky white

after about 10 min. of settling, indicating cessation of flocculation. At this point the residual chlorine ion concentration is low enough so as not to interfere with the next step.

9. Add enough concentrated acetic acid to make the slurry about 0.1M (4%, 1M CH_3COOH /1 kg product). Continue mixing for 30 to 60 min. The color of the product should lighten due to dissolution of the excess Pb added initially. Add an anionic flocculant (0.1 w/o aqueous solution of Hercafloc 821, Dupont Chemical Co.), allow the powder to settle and decant the liquid.
10. Repeat the acid treatment-flocculation-decantation twice.
11. Wash two more times using dilute acetic acid ($1 \times 10^{-3}\text{M}$). Use the minimum amount of flocculant necessary in steps 9, 10 and 11.
12. Dry the slurry by heating at 150°C .
13. The dried powder should be heated in air to about 500°C for about 20 min to remove any remaining water, acetic acid and flocculant. After this treatment it is ready to use.

This procedure was followed with all the LZT compositions discussed in this report.

The objective of the work on powder synthesis was to produce homogeneous powders of controlled stoichiometry whose sintering behavior, as determined by measuring ceramic properties, was reproducible from lot to lot. In pursuit of this objective a number of powder compositions were prepared by this technique. The first of these was a series having varying Zr/Ti ratios around and including the composition $\text{Pb}_{.94}\text{Sr}_{.06}(\text{Zr}_{.53}\text{Ti}_{.47})_{.997}\text{Fe}_{.003}\text{O}_{2.9985}$. This composition is one used to make piezoelectric ceramics which are to be driven at high voltages, such as in sonar applications. Most of the experiments on powder synthesis and sintering technique development were made using these powders.

It was also necessary to determine if many of the other dopants found to be useful in modifying LZT properties could be introduced during molten salt synthesis. Accordingly, a slow aging "driver" type

V. CONCLUSIONS

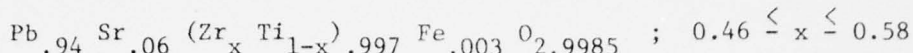
The conclusions that may be drawn from the work done up to the time

of composition developed by Jaffe⁽³⁾ was made up. This was, nominally,

$\text{Pb}_{.94} \text{Ca}_{.05} \text{Mg}_{.01} [(\text{Zr}_{.52} \text{Ti}_{.48})_{.97} \text{Fe}_{.01} \text{Cr}_{.02}] \text{O}_{2.985}$. Also, a series of "hydrophone" compositions were made. These had Zr/Ti ratios around and including $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_{.54} \text{Ti}_{.46}) \text{O}_3 + 1 \text{ w/o Nb}_2\text{O}_5$. The same compositions were also made with Ta, Bi, Sb, As and V replacing Nb on an atom-for-atom basis. The properties of the ceramics made from all of the above mentioned powders are given in Section IV of this report. The chemicals used in the syntheses and their sources are listed in the appendix.

III. POWDER CHARACTERISTICS

The characteristics of molten salt synthesized powders from the composition sequence,



will be described. These powders were all light yellow in color and darkened readily on exposure to light. They were aggregated as seen in Fig. 1. The individual powder grains are rounded in shape and range in size up to about $0.7\mu\text{m}$ as seen in Fig. 2. The powder aggregates are friable and readily break down during pressing except, apparently, in rare exceptions to be described in Section IV A. Fig. 3 shows a typical particle size distribution obtained by measurement with a Coulter Counter. The "particles" are, of course, almost all aggregates.

Chemical analysis for Na and K revealed that the powder contained about 680 ppm Na and about 170 ppm K in solution. These values are to be compared to the figures obtained on a commercial LZT produced by calcination, which were about 115 ppm Na and 30 ppm K. The analyses were performed by atomic absorption after dissolving the powder in hot, concentrated HCl.

The amount of unreacted zirconia was determined by weighing the residue remaining after the powder was dissolved in hot, concentrated HCl. Following the standard recipe for the synthesis resulted in an unreacted zirconia content of about 0.4 weight percent. If the zirconia was mixed with water and then whipped in a blender for about 10 minutes before being added to the other components of the reaction mixture the unreacted zirconia in the final powder dropped to about 0.02 weight percent. This result clearly indicates that large, hard ZrO_2 aggregates in the reaction mixture have to be broken down if complete reaction is to take place in the molten salt. This could also be accomplished by milling the reaction mixture.

The presence of large aggregates in the reaction mixture should be even more troublesome in the case of powders made by calcination. An analysis of a "good" commercial LZT powder⁽⁴⁾ showed a zirconia content of about 1.3 weight percent. In commercial practice it has been found that such a level of unreacted zirconia is generally not associated with poor sintering behavior or difficulty in poling⁽⁵⁾.

The results of examining the as-produced powders with X-rays

can be summarized as follows:

1. No phase other than lead zirconate titanate was ever observed.
2. The peaks in the powder patterns are not sharp, indicating that the powders are not "well crystallized". In addition, judging from the relative intensities of the reflection peaks, the X-ray analyst concluded that disorder exists on the (hk0, h00) planes in the tetragonal phase (but that there is good ordering along the C axis).
3. Judging from the width and structure of the reflections, the X-ray analyst concluded that both the tetragonal and rhombohedral phases were present in the powders having compositions at and around $Zr/Ti = .530/.470$, which is very near the morphotropic rhombohedral-tetragonal boundary on the phase diagram for $PbTiO_3$ - $PbZrO_3$ ⁽⁶⁾. The fact that the X-ray reflections of the rhombohedral and tetragonal phases overlap to a considerable degree coupled with the fact that the single phase reflections themselves are not sharp made it impossible to accurately determine the width of the two-phase field or the lattice parameters of the phases.
4. Differences in the line shapes of the reflections were observed when powders which were prepared in a nominally identical manner were examined.

The uncertainty in the lattice parameters obtained from measurements on the as-made powders can be illustrated by the following results. When samples from 3 batches of powder having $Zr/Ti = .53/.47$ which were synthesized in essentially the same way were analyzed, the tetragonal a and c lattice parameters obtained were 0.404 and 0.411, 0.405 and 0.413, and 0.406 and 0.414 nm, respectively.

IV. PROPERTIES OF CERAMICS

Demonstrating the utility of the powders made by the molten salt technique requires that they be prepared for pressing, pressed and then fired into ceramics. Since the properties of a ceramic depend (sometimes critically) on how these steps are carried out as well as on the composition of the powder, the task of demonstrating the reproducibility of a powder as well as any benefits that might accrue from its anticipated homogeneity is made difficult. In the work reported here, a number of powder preparation and firing techniques were tried as the powder synthesis technique was being developed. The objective was to obtain some knowledge of the behavior of the powder, improve the synthesis technique, and to establish a procedure for producing ceramics of reasonable density that could be compared to each other and to ceramics produced from other powders. No intensive effort was made to optimize the properties of the ceramics of any particular composition as it was judged that such an effort should more properly be made later after the more general behavior of the powder during firing was known. As was mentioned previously (Section II) most of the work on ceramic preparation techniques was done, using powders having Zr/Ti ratios around that of the composition $\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_{.53} \text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$.

A. Powder Preparation and Pressing

In order that warpage not occur when a green body made of pressed powder is fired the body must, in general, have a high and uniform green density so that the shrinkage is isotropic and relatively small. The green body must also have sufficient strength to withstand any necessary handling. The processing steps required to achieve such a green state depend on the nature of the powder, i.e. the size distribution of the particles and particle aggregates and their mechanical strength, and the size and shape of the body. The latter affects the way that the pressing pressure is distributed throughout the body.

Samples for this investigation were pressed in a Carboly die of 2.54 cm diameter. About 5g of powder were loaded and pressed at 69 MPa (10 Kpsi) holding 1 minute at pressure. This yielded a green body of about 2.5 mm thickness. In order to insure uniform density, these discs were then placed in a rubber bag, immersed in oil, and

isostatically pressed at around 340 MPa (50 Kpsi). When as-made powder was pressed in this manner it was observed that the discs were somewhat fragile and that even though the final density of the fired discs was high ($> 7.6 \text{ Mg/m}^3$) they contained a few very large pores. These pores had the appearance of having originated from large aggregates of particles which did not break down during the pressing.

Accordingly the procedure was adopted to incorporate stearic acid as a pressing lubricant into the as-made powder to achieve better particle packing. Two weight per cent was chosen as the near minimum amount that resulted in a green body having adequate strength. The stearic acid was incorporated into the powder by dissolving it in benzene, adding to the powder, then milling the mixture for about 24 hours in a polyethylene jar using stabilized zirconia balls. This procedure broke down any hard aggregates. The milling time used happened to be convenient. A shorter time would serve as well.

The mixture was then poured into an open beaker and the benzene evaporated by applying heat. The powder was stirred constantly during drying to prevent stratification or segregation of the stearic acid in the powder as its solvent evaporated. The dry powder was then passed through a 60 mesh nylon screen after which it was ready for pressing. The densities of green bodies pressed from such powder were found to be around 5.7 Mg/m^3 . The final densities of fired bodies were not significantly greater than those pressed from as-made powder but they were free of any large pores.

Stearic acid was chosen as the lubricant because it can be completely burned out of the pressed body at low temperature before final firing at high temperature. Water soluble lubricants such as polyvinylalcohol and methyl cellulose leave residues after burn-out that are rich in sodium and were therefore avoided in this work.

As a result of a considerable number of powder processing and pressing variations that were tried it was concluded that, in order to consistently achieve high density and a uniform microstructure in LZT bodies made from molten salt synthesized powder, a pressing

lubricant should be used along with milling to break up any hard aggregates of particles. The slip should be dried as not to segregate the lubricant. (Besides the method indicated above a freeze drying process has also been successfully used to accomplish this. There is no reason to think that spray drying would not also work satisfactorily). It is important to press the powder hard enough to get a high green density. Although routinely used in the work reported here to insure uniformity, the isostatic pressing step is probably not an absolute requirement to produce satisfactory ceramics.

B. Firing

After pressing, the binder was burned out of the disks by laying them on a powder of their own composition spread on a stabilized zirconia plaque and firing uncovered in air for 1 hour at 600°C. The fractional weight loss during this step was always within the experimental uncertainty of the amount of lubricant added to the powder.

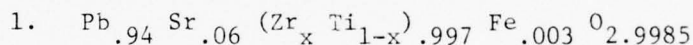
The final firings were done in a box type furnace heated by Globars and having a working space of dimensions approximately 10 x 13 x 25 cm. The samples were heated at a rate of 125°C/hr to 1325°C, held there for one hour, then the power was cut-off and the samples allowed to furnace cool (overnight). Oxygen was bled into the furnace during the entire firing cycle since it is well known that higher densities are achieved when LZT is fired in oxygen than in air. Typical densities achieved were around 7.5 to 7.6 Mg/m³. Separate firings of samples in a small tube furnace where the atmosphere was definitely established at 100% oxygen gave densities around 7.7 Mg/m³. It appears, therefore, that the atmosphere in the box furnace during firing probably contained a significant amount of nitrogen from air leaking into it. The average grain size in all samples was about 4µm.

For firing, the pressed discs of a single composition were placed in a stack of 5 to 6 in a stabilized zirconia crucible. Loose powder of the same composition was placed under, around and over the stack as well as between the individual discs. The crucible was then covered with an alumina disc. All of the alumina

and zirconia ware was "seasoned" before first being used to fire samples by being used to fire loose powder only. Samples fired in the manner typically experienced a weight loss of around 0.3%, part of which can be attributed to a slight chipping of the edges when adhering powder was scraped away after firing.

Some firings were made with the stack of discs placed on a bed of powder spread on a stabilized zirconia plaque. This was then covered with a zirconia crucible. Additional control of the atmosphere of volatile PbO was effected by sometimes including "donor blocks" made of pressed, unreacted powders of PbO and ZrO_2 in the weight ratio 2.3/1. This is essentially the same as the method used commercially to control the lead content of LZT ceramics during firing. It was found in these experiments that the presence of donor blocks did reduce weight loss, indeed a weight gain was sometimes observed, but there still remained a top-to-bottom variation in the weight changes of the discs in the stack. It was therefore in the interests of sample uniformity that the previously described method of firing the discs while buried in powder was adopted.

C. Ceramic Properties



A number of ceramics were made from powders having compositions given by the general formula $\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_x \text{Ti}_{1-x})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$. Iron enters LZT in the trivalent state and occupies the B sites in the ABO_3 perovskite structure⁽⁷⁾. Table I lists the X-ray lattice parameters of ceramics with increasing x in the general composition formula. The X-ray diffraction patterns of powder samples prepared from these ceramics show sharp lines indicating homogeneous, well crystallized materials. In this respect they differ markedly from the diffraction patterns obtained from the as-prepared powder which, as previously described (Section III), indicates the presence of a considerable degree of crystal disordering.

The progressions of the lattice parameters with x shown in Table I show an abrupt change at $x = .530$, where the heretofore purely tetragonal X-ray patterns begin to show the presence of a minor amount of rhombohedral phase. The relative amount of

rhombohedral phase present could not be determined in any of the compositions shown but it is apparent that the phase boundary of the tetragonal field lies between $x = .520$ and $.530$. This is at some variance with what can be deduced from information available from the literature, but there is considerable disagreement between different investigators.

To illustrate, it will be assumed that the small amount of iron present has a negligible effect on the phase diagram in the composition region in question. Ikeda⁽⁸⁾ determined the room temperature phase diagram for the system $\text{PbTiO}_3\text{-PbZrO}_3\text{-SrTiO}_3\text{-SrZrO}_3$. When no strontium was present he placed the "phase boundary" between the tetragonal and rhombohedral phases (the composition at which the phases were present in equal amounts, and called the "morphotropic phase boundary" in LZT because of its near independence of temperature) at about $x = .570$. For 6 a/o strontium the boundary was at about $x = .585$. However, in a late version of the phase diagram for the system $\text{PbTiO}_3\text{-PbZrO}_3$, the morphotropic phase boundary is put at $x = .535$ ⁽⁶⁾. In still more recent work⁽⁹⁾ on this same system it was determined that the two phase field extended from $x = .49$ to $.61$ with the lever law applying and thus only the relative proportions of the phases but not their lattice parameters changing in this range. This would put the morphotropic phase boundary at $x = .55$. This work was strongly attacked by Isupov⁽¹⁰⁾ who argued from his experimental results that no true two-phase region exists in this system but that there is an overlap region between the tetragonal and rhombohedral fields, consequently the lattice parameters measured for the phases in this region depend on the composition. In his reply, Benguigui⁽¹¹⁾ argues that Isupov is incorrect in principle and that his (Isupov's) experimental results may be due to the presence of non-equilibrium, metastable phases arising from too rapid cooling of samples.

This brief discussion illustrates that there is still considerable uncertainty about the details of the phase diagrams for the $\text{PbZrO}_3\text{-PbTiO}_3$ + dopant systems. Some of the differences between observers may arise from different methods of making the powder and/or firing the ceramics. The data shown in Table I are not, of course, sufficient to resolve any of the questions. It would

appear, however, to be a valuable exercise to obtain more such data on ceramics made from molten salt synthesized powders. Such data for specimens in the range between $x=.560$ and $.600$ is now being obtained to establish the upper boundary of the two phase field.

According to the literature, all of the electrical and piezoelectric properties of LZT show a variation with composition. That of the post-poling dielectric constant (K_{33}) and the planar coupling coefficient (k_p) is particularly dramatic, with both peaking sharply close to the tetragonal side of the morphotropic phase boundary at room temperature⁽¹²⁾. Fig. 4 shows the values obtained for these properties on the ceramics made during this investigation. Reasoning by analogy, the morphotropic phase boundary of LZT made from the molten salt synthesized powders should lie at around $x=.545$. Fig. 5 shows the composition variation of the piezoelectric coefficient d_{31} .

The poling procedure used in this investigation was to apply fired-on silver paste electrodes to the discs and to pole them at 120°C in a bath of Fluorinert (Minnesota Mining and Manufacturing Company) using a field of 2.36 MV/m (60 V/mil). The field was applied for 3 periods of 5 minutes each with a reversal of direction after each of the first 2 periods. Dielectric constant and dissipation factor (loss tangent) at 1 KHz were measured using a General Radio Co. 1615 Capacitance Bridge. The piezoelectric properties were measured using the resonance technique⁽¹³⁾.

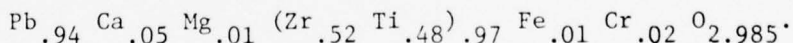
The ability of different batches of molten salt synthesized powders to be fired into ceramics having properties lying in a narrow range was investigated simultaneously with the work on the development of the synthesis technique and the investigation of pressing and firing. This was necessary because reproducibility of ceramic properties was one of the indicators of good synthesis and processing technique. Table II lists data on the one hour post-poling dielectric constant and planar coupling coefficient which illustrate the state of development of the reproducibility property over about the second half of the contract period. These data were obtained on samples from 5 batches of powder having the composition $\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_{.53} \text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$. The synthesis

techniques used differed in minor respects for the different batches. The samples were also not all fired under the same conditions of atmosphere control in the furnace or in the method used to establish the PbO atmosphere in the closed crucible containing the samples. They were all, however, fired according to the same temperature-time schedule and had the same poling treatment. These samples therefore embody more a priori variability than will be allowed in batch reproducibility experiments that will be conducted using standardized synthesis, pressing and firing techniques which are now better developed.

The composition of these batches is that of a "hard" LZT whose properties are expected to lie between those of Military Standard Type I and Type III (Vernitron's PZT-4 and PZT-8) because of the relatively small iron content. Table III shows the average results of measurements⁽¹⁴⁾ made on 3 discs of this composition about 10 days after poling. (The aging rates represent values taken over about 40 days). These results indicate that this composition made very good piezoelectric ceramic, particularly notable for very low losses at both high and low driving fields, high mechanical Q and relatively small change in dielectric constant at high driving field. In general these ceramics, whose Fe content is about one-half that usually added to the base composition to reduce losses under high driving voltage, have the higher K_{33} and d_{33} associated with Type I ceramics along with the low Tan Δ under high drive associated with Type III's.

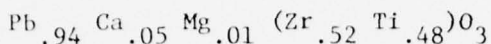
2. Slow Aging Composition

Another powder composition whose synthesis by the molten salt technique was undertaken was that of a slow aging Type I material reported by Jaffe⁽³⁾ to be



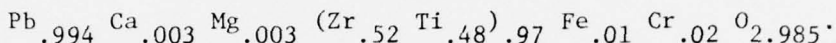
Chemical analyses of the resultant powder indicated the presence of Fe and Cr in about the right amount. The Ca and Mg, however, were found to be present only to a level about 1/16 and 1/2.8 of that indicated by the formula. Substantially the same content

of Ca and Mg was also found when the synthesis of a powder having the nominal composition



was attempted. Loading the reaction mixture with an excess of CaCO_3 and MgOH_2 to a level 10 times that given in the formula resulted in more Mg and Ca being found in the powder by chemical analysis but the Xray diffraction patterns also showed the presence of new phases, one of which was identified as CaTiO_3 .

The results imply that the solubility limit of Ca and Mg in this compound is substantially less than indicated by the nominal formula. The composition formula for the slow aging ceramic is therefore probably closer to



These indications of limited solubility are in accord with observations made at NRL⁽¹⁵⁾ indicating the presence of Ca in the grain boundaries of slow aging ceramics of the nominal composition.

The ceramics made from the molten salt synthesized powder had to be fired at 1225°C to avoid all the samples in the stack being welded together along with the surrounding powder. The properties of the ceramics differed considerably from those reported by Jaffe for his. Whereas Jaffe gave 1200 and -0.5%/decade for K_{33} and its aging rate, and similarly 0.47 and -0.2%/decade for k_p , the values obtained on ceramics made from the molten salt synthesized powders were 900 and 1%/decade for K_{33} , and .35 and 0.2%/decade for k_p . These differences may be caused by the different total Ca and Mg contents and their distribution in the ceramic.

3. $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ + additives

A number of elements which commonly exhibit valence states of +3 and +5 were incorporated into three base compositions of LZT.

The base compositions were:

Composition A; $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_{.52} \text{Ti}_{.48})\text{O}_3$,

Composition B; $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_{.54} \text{Ti}_{.46})\text{O}_3$,

Composition C; $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_{.56} \text{Ti}_{.44})\text{O}_3$.

Composition A is on the tetragonal side of the morphotropic phase boundary and exhibits an increase in dielectric constant on poling. The other two compositions are on the rhombohedral side of the boundary and experience a decrease in dielectric constant on poling.

The elements added were introduced into the reaction mixture as the following oxides; Nb_2O_5 , Sb_2O_3 , Ta_2O_5 , Bi_2O_3 , V_2O_5 and As_2O_3 . The amount of Nb_2O_5 added was 1 w/o of the base composition, which is equivalent to 2.4 a/o substitution of Nb for Zr and Ti. All the other oxides were introduced in quantities which, for the cations, were atom-for-atom identical to the Nb_2O_5 additions.

The ceramics made from the powders fell into two classes. The first class, which included all of the compositions made with added Bi, As and V, quickly arced over when an attempt was made to pole them at a field of 2.36 MV/m (60 v/mil) at 120°C. The highest poling field these specimens could withstand at 120°C (which was the only temperature tried) was 1.18 MV/m (30 V/mil). The values of k_p achieved were small, typically less than 0.1. In the case of the As and Bi additions, the change in dielectric constant on poling was positive for base compositions A and B, and negative for base composition C. In the case of the V addition the change was negative for all base compositions. Also, the samples with added As and V had to be fired at 1250°C because at the usual 1325°C the stack of discs and the surrounding powder in the crucible sintered into a hard, nearly inseparable mass.

The second class of ceramics was composed of all the compositions made using Nb, Sb and Ta as additives. These all could be poled at 2.36 MV/m and 120°C in the usual way. Table IV lists some of the properties of these ceramics one hour after poling. In all cases the ceramics based on compositions A and B showed an increase in dielectric constant on poling while the ceramics based on composition C showed a decrease.

The results for the Nb addition are in general agreement with those of Kulcar⁽¹⁶⁾ who found the beneficial effects of this additive on K_{33} , k_p and d_{31} to be greatest at the B composition. In comparing Kulcar's results for Nb and Ta added to composition B with the ones in Table IV, and taking account of the fact that Kulcar's values are for

1 hour after poling, it was seen that the K_{33} values are about alike, Kulcar's k_p 's were 20 to 30 per cent higher, his d_{31} for Ta addition was about 50 per cent higher, his dissipation factor ($\tan \Delta$) was about twice as big and his mechanical Q (Q_m) was about 1/4 as big. It should be noted that Kulcar poled at a field of 4 MV/m, but no temperature is given so it is not possible to judge if this can account for the difference k_p and d_{31} . Over all, it can be stated that the ceramics made from the molten salt synthesized powder appear to be appreciably less lossy than those made by Kulcar.

From the data in Table IV is apparent that Sb has the same general effect on the properties of the base compositions as do the additives Nb and Ta. No data was found in the literature to compare with these results. Nor could any data be found to compare with the observations on the ceramics doped with V and As. Haertling⁽¹⁷⁾ reports on hot pressed samples of a composition containing 2 a/o Bi, namely $Pb_{.99} (Zr_{.53} Ti_{.47})_{.98} Bi_{.02} O_3$, in which he assumed that the Bi went into the structure as a pentavalent ion replacing Zr or Ti. He reports k_p 's of around 0.6 and a decrease in dielectric constant on poling, but gives no information on the poling conditions. Atkin et al⁽¹⁸⁾ have shown that Bi enters LZT of this base composition as a trivalent ion replacing Pb, while Nb goes in pentavalently for Zr or Ti.

V. CONCLUSIONS

The conclusions that may be drawn from the work done up to the time of this report are as follows:

1. The molten salt synthesis technique for producing LZT powders has been developed. It has been demonstrated that powders of all the technologically important compositions can be made by this method. The powders can be made so as to contain unreacted material on the level of a few hundredths of a per cent. The size distribution and strength of the particle aggregates in the powders is such that they are easily prepared for pressing and firing into bodies having high density.
2. Ceramics made from molten salt powders generally have smaller loss tangents and higher mechanical Q values than those reported for ceramics made from calcined powders.
3. The degree of reproducibility of ceramic properties for identical processing and firing of different lots of identically synthesized powder remains to be definitively established.

VI. FUTURE WORK

During the next period of work under this contract a definitive assessment of the reproducibility of ceramics made from molten salt synthesized powders will be made. Four batches of powder of composition $\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_{.53} \text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$ have already been synthesized under identical conditions. Samples made from these batches will be pressed and fired in various combinations under identical conditions to obtain the required information.

The effect of firing time, temperature and atmosphere on the microstructural, electrical and piezoelectric properties of LZT ceramics will be investigated. Since it is well known that changes in lead content occur during firing and have a considerable effect on properties, a precise analytical method for lead analysis will be developed and applied during this investigation. Samples will be examined by optical microscopy to characterize their microstructures. Also, the electron microprobe will be used to investigate any compositional variations that may occur near grain boundaries. The aging behavior of the ceramics will be of particular interest during the investigation.

The compositions initially chosen for this continuing study are:

$\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_{.53} \text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$,

$\text{Pb}_{.939} \text{Sr}_{.049} (\text{Zr}_{.54} \text{Ti}_{.46})_{.976} \text{Nb}_{.024} \text{O}_3$,

and the slow aging composition nominally given (Section IV C2) as

$\text{Pb}_{.994} \text{Ca}_{.003} \text{Mg}_{.003} (\text{Zr}_{.52} \text{Ti}_{.48})_{.97} \text{Fe}_{.01} \text{Cr}_{.02} \text{O}_{2.985}$.

Variations of these compositions will be investigated as seems appropriate.

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APPENDIX

Reactants Used in LZT Syntheses

Antimony Trioxide - Sb_2O_3 - Mallinckrodt-Analytical Reagent

Arsenic Trioxide - As_2O_3 - Fisher Scientific Co. - Certified A-59

Bismuth Trioxide - Bi_2O_3 - J. T. Baker Co. - Reagent

Calcium Carbonate - CaCO_3 - Mallinckrodt - Analytical Reagent 4072

Chromium Oxide - Cr_2O_3 - Allied Chemical - Purified Code 1581

Ferric Oxide - Fe_2O_3 - Fisher Scientific Co. - Certified I-116

Lead Oxide - PbO - Fisher Scientific - Certified L-71

Magnesium Hydroxide - $\text{Mg}(\text{OH})_2$ - Mathewson, Coleman and Ball
Reagent Powder

Niobium Pentoxide - Nb_2O_5 - Ciba - Optical Grade I (>99.9%)

Potassium Chloride - KCl - J. T. Baker Co. - Reagent

Sodium Chloride - NaCl - J. T. Baker Co. - Reagent

Strontium Carbonate - SrCO_3 - Matheson Coleman and Ball
Reagent SX1010 CB780

Tantalum Pentoxide - Ta_2O_5 - Research Organic/Inorganic Chemical Corp. -
99.99% pure - TA207

Titanium Dioxide - TiO_2 - Fisher Scientific Co. - Certified T315

Vanadium Pentoxide - V_2O_5 - Fisher Scientific Co. - Certified V7

Zirconium Dioxide - ZrO_2 - Reactive Metals Inc. - Reactor Grade
99.5% pure

Table I
X-RAY LATTICE PARAMETERS FOR LZT CERAMICS
HAVING THE GENERAL FORMULA
 $\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_x \text{Ti}_{1-x})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$

TETRAGONAL LATTICE CONSTANTS

<u>X</u>	<u>a</u> <u>nm</u>	<u>c</u> <u>nm</u>	<u>Other Phases Present</u>
.400	.3977	.4088	
.470	.4030	.4125	
.480	.4031	.4124	
.490	.4040	.4128	
.500	.4048	.4126	
.510	.4051	.4126	
.520	.4055	.4127	
.530	.4054	.4117	Minor Rhombohedral
.540	.4059	.412	"
.550	.4063	.4102	"
.560	.4071	.4101	"
.600	.5746	.7074	Sample Rhombohedral-- Equivalent Hexagonal Parameters Given

Table II

POST-POLING VALUES OF DIELECTRIC CONSTANT (K_{33}) AND PLANAR
COUPLING COEFFICIENT (k_p) OF CERAMICS MADE FROM
DIFFERENT BATCHES OF POWDER HAVING THE COMPOSITION

$\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_{.53} \text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$

SEE TEXT FOR DETAILS.

<u>Batch</u>	<u>No. of Samples</u>	<u>K_{33}</u>	<u>k_p</u>
29	24	1284 ± 40	$.537 \pm .027$
30	9	1211 ± 64	$.516 \pm .030$
30A	2	1124 ± 9	$.448 \pm .015$
30B	1	1201	.481
30C	3	1219 ± 26	$.492 \pm .013$

Table III
AVERAGE VALUES OF THE PROPERTIES
OF 3 SAMPLES OF COMPOSITION
Pb.₉₄ Sr.₀₆ (Zr.₅₃ Ti.₄₇).₉₉₇ Fe.₀₀₃ O_{2.9985} .

Density	7.5 Mg/m ³
K ₃₃ (1 KHz)	1200
Tan Δ (1 KHz)	0.0002
k _p	0.52
Mechanical Q	1700
d ₃₃	250 x 10 ⁻¹² C/N
% change in K ₃₃ per time decade	-4.0
% change in k _p per time decade	-1.6
Tan Δ at 0.39 MV/m	0.01
% change in K ₃₃ at 0.39 MV/m	+4.5

Table IV

ONE HOUR POST-POLING PROPERTIES OF SEVERAL BASE
COMPOSITIONS OF LZT WITH 2.4 ATOM PERCENT ADDITIVES.

BASE COMPOSITIONS: A, $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_{.52} \text{Ti}_{.48}) \text{O}_3$;
B, $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_{.54} \text{Ti}_{.46}) \text{O}_3$; C, $\text{Pb}_{.95} \text{Sr}_{.05} (\text{Zr}_{.56} \text{Ti}_{.44}) \text{O}_3$.

Added Atom	Base Comp.	Density (Mg/m^3)	K_{33}	k_p	$\tan \Delta$	$-d_{31}$ ($\text{C}/\text{N}) \times 10^{-12}$	Q_M
Nb	A	7.30	1343	.338	.008	84	280
	B	7.35	1788	.468	.009	127	248
	C	7.33	1135	.399	.02	86	142
Sb	A	7.57	1260	.308	.011	61	185
	B	7.55	1807	.385	.014	106	151
	C	7.61	988	.268	.023	51	121
Ta	A	7.55	1160	.287	.006	57	396
	B	7.63	1534	.412	.008	99	275
	C	7.64	962	.498	.011	95	161



Figure 1. Aggregated, Molten Salt Synthesized LZT Powder. SEM, 1000X.

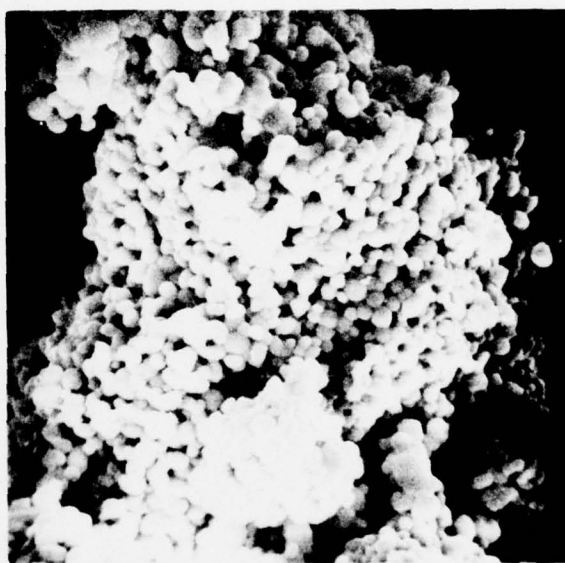


Figure 2. Detail of LZT Powder Aggregate. SEM, 5000X.

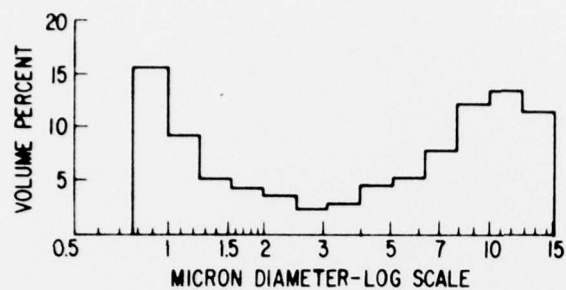


Figure 3. Particle Size Distribution Typical of Those Obtained On Molten Salt Synthesized LZT Powders By Coulter Counter Measurement

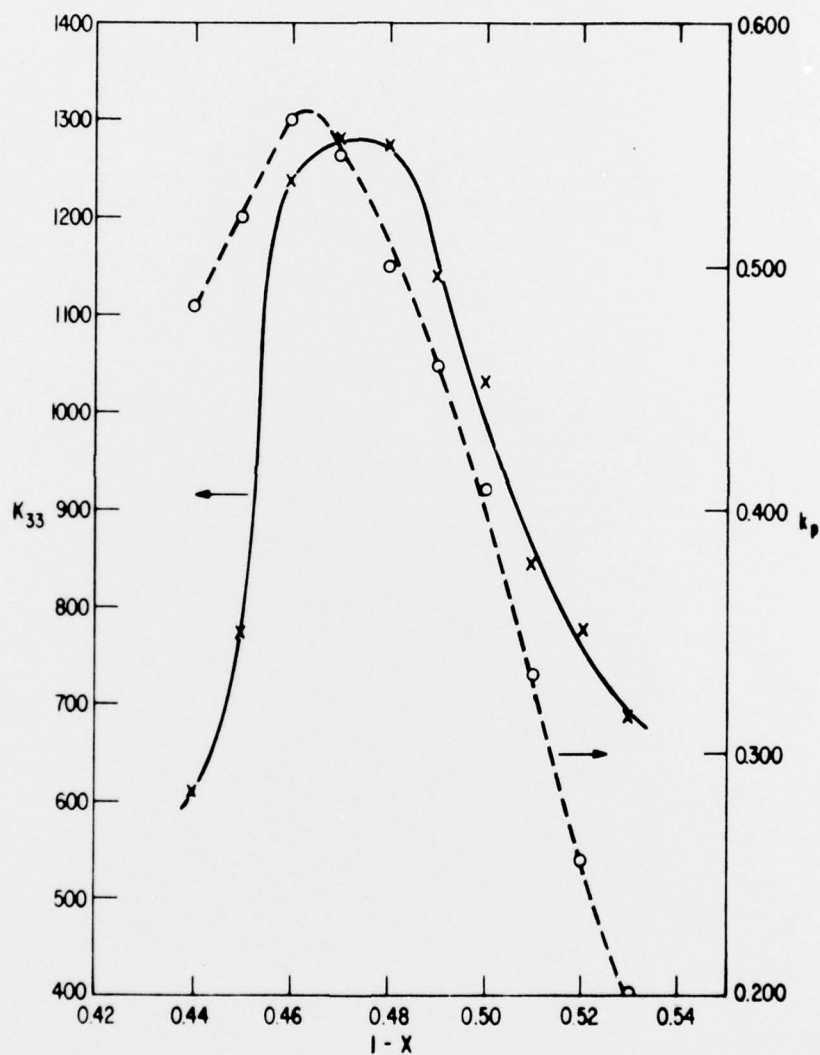


Figure 4. Room Temperature, One Hour Post-Poling Dielectric Constant (K_{33}) at 1 KHz and Planar Coupling Coefficient (k_p) Versus Composition for Ceramics Having the General Formula $\text{Pb}_{.94}\text{Sr}_{.06}(\text{Zr}_x\text{Ti}_{1-x})_{.9997}\text{Fe}_{.003}\text{O}_{2.9985}$

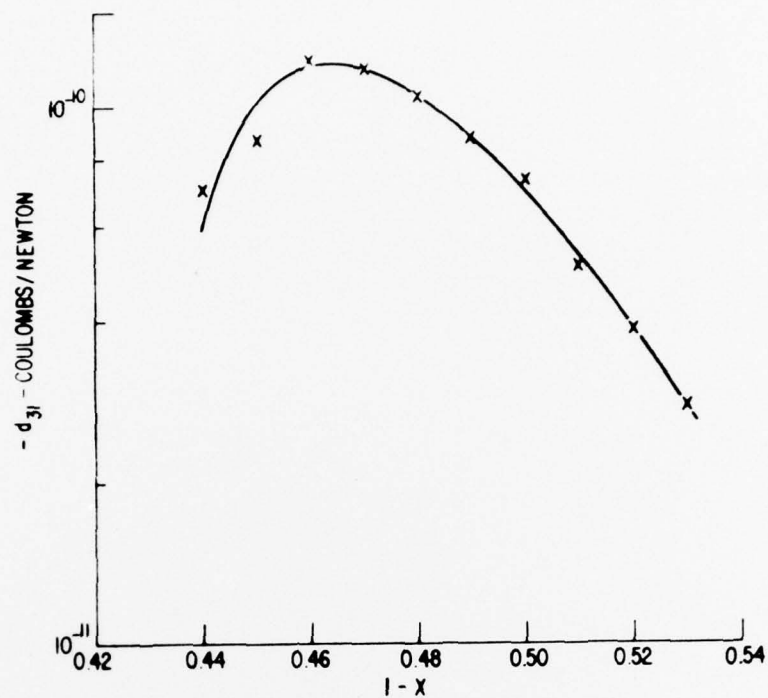


Figure 5. d_{31} Versus Composition for Ceramics Having the General Formula $\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_x \text{Ti}_{1-x})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$

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